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MÖSSBAUER EFFECT STUDIES ON FROZEN SOLUTIONS

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MÖSSBAUER EFFECT STUDIES ON FROZEN SOLUTIONS

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SUMMARY

Mössbauer studies of frozen solutions have furnished valuable information about the structure of ions in frozen systems. The efforts achieved in these field are reviewed. Although during the past ten years many apparently anomalous phenomena could be satisfactorily explained, some interesting new results could be expected from further investigations.

New results on $FeCl_2$, $FeBr_2$, FeI_2 frozen aqueous solutions are included in the paper. The role of the glass former was clarified. In $FeBr_2 \cdot 6H_2O$ at 20°C a phase transformation was observed. The experiments on hexacyanoferrate frozen solutions showed that the solute complex crystallises out from the solution during the cooling process unless glycerol is added to the solution.

The observed chemical reaction in aquopentacyanoferrate aqueous solution makes questionable the postulated dimerization of these molecules.

A compilation of the possible applications of the results obtained so far is given.

РЕЗЮМЕ

Измерения, выполненные в замороженных растворах с помощью эффекта Мессбауэра, предоставляют ценную информацию о структуре ионов, находящихся в этих системах. Настоящая работа содержит краткое изложение ранее проведенных исследований. Хотя за последние десять лет большое количество аномальных эффектов, наблюдаемых в системе растворов, получило объяснение, дальнейшие исследования безусловно обещают интересные результаты. В данной работе приведены результаты исследований, полученные автором при изучении замороженных растворов $FeCl_2$, $FeBr_2$ и FeI_2. Выяснена роль стеклообразователя, добавленного к раствору. В случае соединений $FeBr_2.6H_2O$ при температуре -20°C обнаружен новый, до сих пор неизвестный фазовый переход.

Установлено, что в случае водных растворов Fe/II/ и Fe/III/ растворенное комплексное соединение выкристаллизовывается из раствора в процессе замораживания, если раствор не содержит стеклообразователя /глицерин/. Исследования химической реакции аквапентационида железа /II/ в водных растворах с помощью эффекта Мессбауэра поставили под вопрос существование ранее предложенного процесса димеризации указанных комплексных молекул.

В конце статьи перечислены дальнейшие возможности прменения методики замораживания растворов.

KIVONAT

A Mössbauer-vizsgálatok értékes információt szolgáltattak a lefagyasztott oldatokban levő ionok szerkezetéről. A jelen cikk tartalmazza az eddig elvégzett vizsgálatok rövid ismertetését. Bár az elmult tiz év alatt ezen oldatrendszereknél megfigyelt több anomális effektust sikerült értelmezni, a további vizsgálatoktól is értékes eredmények várhatók. A dolgozat ismerteti a $FeCl_2$, $FeBr_2$, FeI_2 lefagyasztott oldatrendszereken - a szerző által végzett - legujabb vizsgálatokat. Az oldatokhoz adott üvegképző anyag szerepe tisztázódott a vizsgálatok során. A $FeBr_2 \cdot 6H_2O$ vegyület esetén egy eddig nem észlelt fázisátalakulást figyeltünk meg -20°C közelében.

A vas/II/ és vas/III/ hexacianid vizes oldatok tanulmányozása azt mutatta, hogy a lefagyasztás során az oldott komplex kikristályosodik az oldatból, ha üvegképző anyagot /glicerin/ nem tartalmazott az oldat.

A Mössbauer-effektus segitségével megfigyelt kémiai reakció a vas/II/ akvapentacianid vizes oldatai esetén kétségessé tette ezen komplex molekulák korábban feltételezett dimerizációját. A cikk végén a lefagyasztott oldatok alkalmazásainak további lehetőségeit soroljuk fel.

1. INTRODUCTION

Very few studies were made on frozen solutions until 1963. Most of the work was carried out below the melting point of the ice and was devoted to the determination of solubilities and eutectic melting points of water-salt systems, in other words, on solvent-salt systems kept in thermodynamical equilibrium and with fast cooling or heating avoided. Measurements were not made far below the eutectic melting point.

Several studies were made on the electron exchange between ions in different oxidation states in frozen solution [1]. In frozen aqueous uranyl nitrate an anomalous sudden decrease (∿20%) of the fluorescence intensity was observed at about -90°C [2]. In irradiated frozen ferrous salt solutions a sudden rise was observed in the $Fe^{2+} \rightarrow Fe^{3+}$ radiooxidation yield at about -90°C. No explanations of these anomalous effects were given.

Mössbauer measurements on fast-frozen solutions date from 1962-64. Kerler, Neuwirth, Fluck and Zimmerman [3], Hazony and Bukshpan [4] and we in Budapest [5] published the first results. Bernas and Langevin [6] reported on Mössbauer studies on vitreosil $FeCl_3$, that is, a highly concentrated frozen $FeCl_3$ aqueous solution. Numerous anomalous effects were observed in these systems [6,7] for which consistent explanations could be given only after detailed investigations had been undertaken. The results suggested that the structures and the structural changes occurring at certain temperatures are determined primarily by the solute material. These studies further supported the hypothesis that the structure of the ions in some solutions can be investigated by Mössbauer spectroscopy. This is a matter of considerable importance in view of the serious limitations of the various physical methods in such investigations.

2. A BRIEF SURVEY OF STUDIES MADE UP TO 1970

2.1. Frozen solutions containing ^{57}Fe.

As in other Mössbauer studies, most of the measurements on frozen solutions were concentrated on ^{57}Fe. Numerous investigations were made on

aqueous solutions of the ferrous salts $FeCl_2$, $Fe(ClO_4)_2$, $Fe(NH_4)_2(SO_4)_2$ and $FeSO_4$ [9,10]. The liquid samples were quenched in liquid nitrogen and the Mössbauer spectra were measured at various temperatures. It was found that the quadrupole splittings measured at -190°C were different from the values measured for crystalline ferrous salt hydrates such as $FeCl_2 \cdot 4H_2O$, $Fe(ClO_4) \cdot 6H_2O$ and $Fe(NH_4)_2SO_4 \cdot 6H_2O$. The isomer shifts and quadrupole splittings of the various salt solutions were nearly the same (δ = 1.40; ΔE = 3.20 mm/sec), which suggested that the symmetries around the ferrous ions are the same and independent of the solute anion.

In most of the solutions the Mössbauer parameters, including the recoilless fraction of the gamma rays and the width of the resonance lines, exhibited drastic changes at a certain temperature on heating the sample up from liquid nitrogen temperature /Fig.1/. This abrupt change could be observed in most cases at about -90°C, which coincides with the temperature of the cubic → hexagonal phase transition in ice and in the early stages of the investigations led to the interpretation that the ice phase transformation could explain the observed anomaly. The coincidence, however, turned out to be "accidental". The transition temperature of the $Fe(NH_4)_2(SO_4)_2$ frozen solution (-60°C) did not support the hypothesis, and furthermore differential thermal analysis /DTA/ [11,12] and proton magnetic resonance studies of the frozen systems [13] demonstrated that only a small proportion of the water content is involved in the transformations.

The result of a typical DTA measurement on $FeCl_2$ frozen solution is shown in Fig. 2. The curve exhibits a single exothermic and two endothermic peaks /numbered 1, 2 and 3, respectively/. Peaks 1 and 2 can be directly related to the changes observed in the Mössbauer parameters. The exothermic peak corresponds to a recrystallisation, the endothermic peaks to melting of $FeCl_2 \cdot xH_2O$ - water eutectic and of ice, respectively. The Mössbauer parameters change abruptly near to the temperature value at which the recrystallisation and melting can be observed. The change can, therefore, be explained by the recrystallisation of the solute material at -80°C to form a new compound, melting at -45°C.

These observations led to the conclusion that after cooling to liquid nitrogen temperature the solid fraction containing the solute salt has a similar or identical structure to a glass phase. This glass phase melts at -120°C and from this a crystalline ferrous salt hydrate crystallizes out. Ruby, Zabransky and Stevens [15] constructed the phase diagram of the $FeCl_2$ - water system using the Mössbauer and DTA results.

A definite correlation was likewise found between the results of the thermal analysis of $FeSO_4$, $Fe(NH_4)_2(SO_4)_2$, $Fe(ClO_4)_2$ frozen solutions and

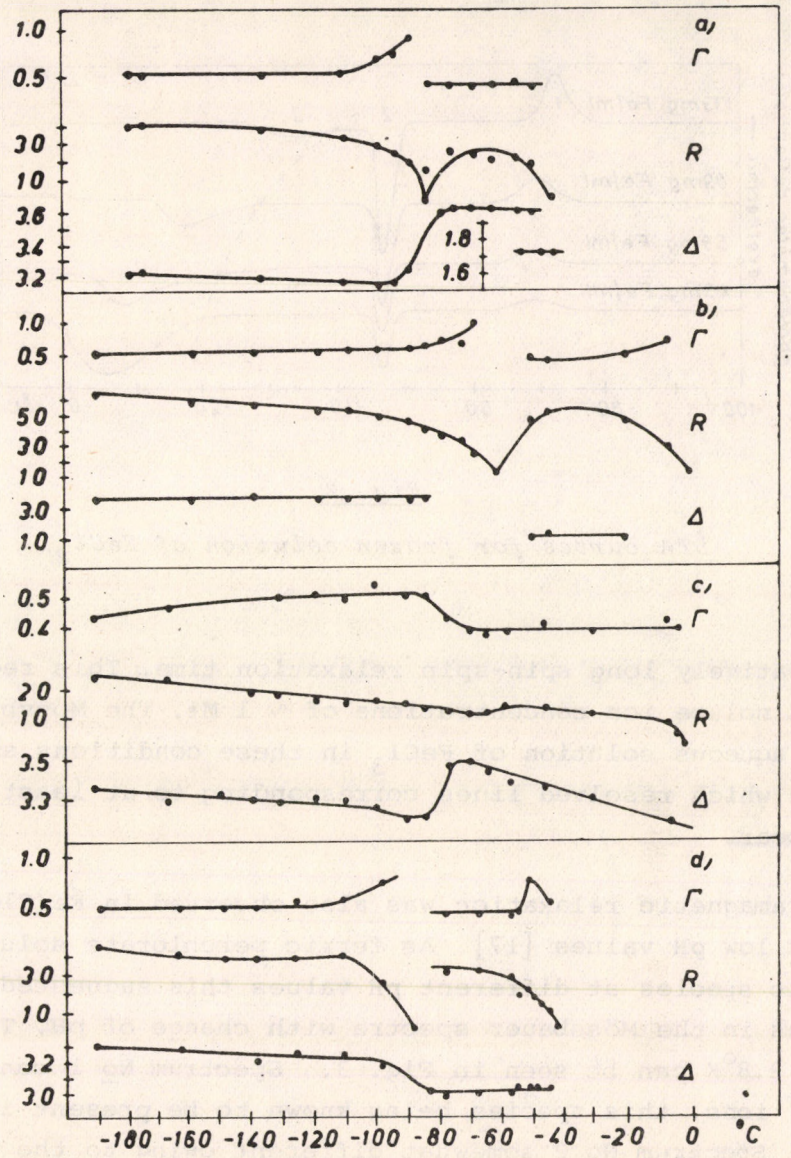

Fig. 1

Temperature dependence of the Mössbauer parameters of frozen $FeCl_2$(a), $Fe(NH_4)_2(SO_4)_2$(b), $FeSO_4$(c) and $Fe(ClO_4)_2$(d) solutions. Γ: linewidth; R: intensity of the ME; Δ: quadrupole splitting.

their Mössbauer data. The various salt solutions, however, show a number of special properties, which have to be treated separately.

Nozik and Kaplan [16] were the first to report studies on $FeCl_3$ aqueous solutions. Here the high-spin Fe^{3+} ion is in a $^6S_{5/2}$ state. Now, it is well known that the spin relaxation time can only be large enough to allow observation of the paramagnetic relaxation effect in dilute paramagnets provided the concentration of paramagnetic ions is low enough to

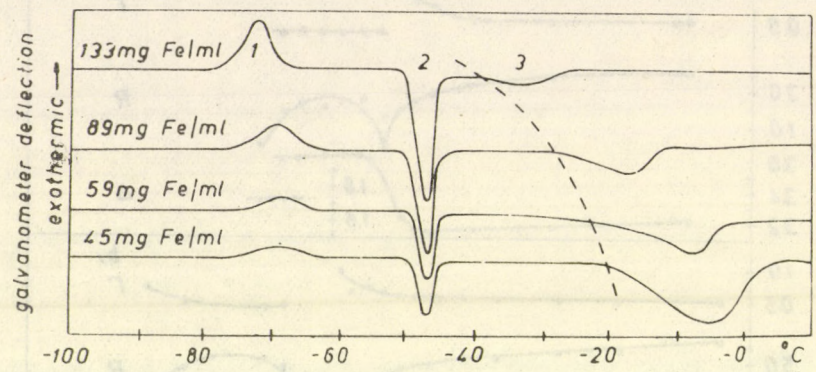

Fig. 2

DTA curves for frozen solution of $FeCl_2$

ensure a relatively long spin-spin relaxation time. This requirement is fulfilled at solute ion concentrations of ∿ 1 M%. The Mössbauer spectrum of a frozen aqueous solution of $FeCl_3$ in these conditions shows a hyperfine structure in which resolved lines corresponding to at least two Kramers doublets appear.

Paramagnetic relaxation was also observed in $Fe(ClO_4)_3$ frozen solutions at low pH values [17]. As ferric perchlorate solutions contain various ionic species at different pH values this suggested there should be variations in the Mössbauer spectra with change of pH. The spectra measured at 2.8°K can be seen in Fig. 3. Spectrum No 1 can be attributed to $Fe(H_2O)^{3+}$ ions, this species being known to be present in solution at pH = O [18]. Spectrum No 2 somewhat different owing to the appearance of well-resolved lines in the central part of the pattern. The paramagnetic splitting was found to be 570 kOe for both samples, a value which can be attributed to the ±5/2 Kramers doublet state [18]. The appearance of the central, roughly triangular, poorly resolved part in the spectrum can be explained by the clustering of the solute ferric ions during the cooling process. The ions get closer to each other and consequently the spin-spin relaxation time decreases; but as its value varies from site to site a poorly resolved hyperfine structure results. The observation of this poorly resolved spectrum is itself evidence of the tendency of the solute ions to separate from ice during the freezing process. At pH ∿ 1, because of the hydrolysis of the $Fe(H_2O)_6^{3+}$ species, a spectrum of the hydrolysis products appears [17].

The different Mössbauer spectra of high-spin Fe^{2+} and Fe^{3+} ions permit the study of electron exchange between the two ions in solution. A suitable technique is to dissolve in water a ferric compound prepared from

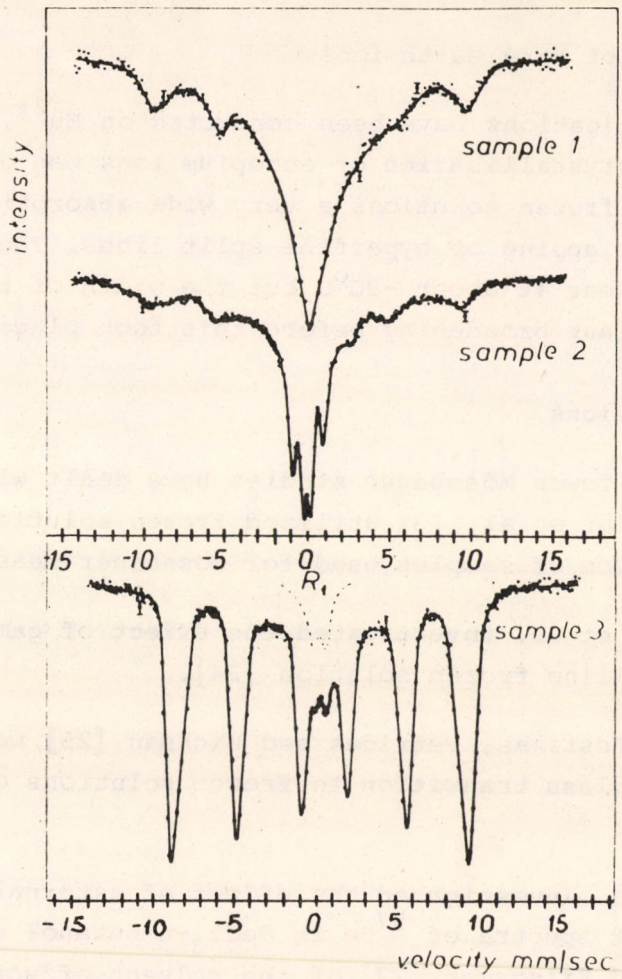

Fig. 3

Mössbauer spectra of $Fe(ClO_4)_3$ frozen solutions at T = 2.8°K pH values: sample 1 pH = 0.5; sample 2 pH = 1.5; sample 3 pH = 2.3

enriched ^{57}Fe along with the ferrous salt containing natural ion. The appearance of the Mössbauer spectrum of the ferrous ion directly show that electron exchange actually occurs in the solution [20].

2.2. Frozen solutions containing ^{119}Sn.

Studies of the Mössbauer spectra of $SnCl_2$ and $SnCl_4$ frozen solutions [21,22] demonstrated that the intensity of the Mössbauer effect decreases to zero at about -90°C. Ruby et al. showed that the coordination of Cl^- ions to Sn^{2+} ions takes place at high concentration [22]. It is known that in less acid solutions Sn^{2+} and Sn^{4+} hydrolyse to tin oxides and hydroxides containing variable quantities of water in the crystal lattice. Therefore, the pH has to be kept low. But this case the system becomes complicated because of the high concentration of different ions.

2.3. Frozen solutions of rare earth ions.

So far investigations have been conducted on Eu^{2+}, Eu^{3+} [23] and Dy^{3+} [20]. The recrystallisation of europium ions was observed at -58.2°C. In 0.4 at % $Dy(ClO_4)_3$ frozen solutions a very wide absorption line was observed due to the overlapping of hyperfine-split lines. The Mössbauer effect was observed to disappear at about -90°C but the width of the line made it impossible to discern any broadening before this took place.

2.4. Non-aqueous solutions.

Considerably fewer Mössbauer studies have dealt with non-aqueous frozen solutions. Kerler et al. (3) utilized frozen solutions to avoid the preferential orientation of samples used for Mössbauer measurements.

Kósa-Somogyi et al. investigated the effect of gamma irradiation on $FeCl_3$ - dimethylaniline frozen solution [24].

Simopoulos, Kostikas, Petrides and Wickman [25] were able to directly observe the glass transition in frozen solutions of $FeCl_2$ in methanol.

Novikov et al. investigated the effect of external magnetic fields on the hyperfine-split spectra of ^{57}Fe in $FeCl_3$-n-butanol solution [26]. In studies by Schnorr and Kriegsman [27] of the solvent effect of acetonitrile and benzene on trimethyltinchloride, a definite concentration dependence of the quadrupole splitting was observed.

3. RECENT DEVELOPMENTS

Altough the work described in the previous sections managed to establish valid explanations for various phenomena observed in frozen solutions some unanswered questions still remained for further research. The results obtained suggested that future investigations should be aimed at certain limited groups of solute compounds, because the intercomparison of data obtained for different type of compounds had proved very difficult. Among the outstanding problems were the questions of what is the structure around solute ions in the glassy state after quenching? What kinds of ionic motion take place in the glass transition? What is the distribution of the frozen ionic species in the samples? What is the structure of eutectic? For which frozen systems can Mössbauer spectroscopy be used in order to gain information about the ionic structure in solution? Most recent work has been directed to the search for answeres to these questions.

Cohen and West [28] investigated the effect of cooling rate on the structure of frozen $SnCl_2$ samples and showed that the cooling rates normally attainable are not sufficient to prevent the precipitation of crystalline salts unless some glass-former, such as glycerol or propylene glycol is added to the system. These glass formers, it was established, do not cause displacement of water from the first coordination sphere of the tin ions.

Brunot, Hauser, Neuwirth and Bolz [29,30] have made detailed investigations of $FeCl_2$ frozen solution by Mössbauer, X-ray diffraction and differential calorimetric methods. They observed a new effect - an increase in the far-off resonance intensity at the glass transition at - 110 ^{o}C. This they explained in terms of free and hindered rotations of water molecules near the glass transition. The x-ray diffraction was, according to them, sensitively influenced by such motions.

Cameron, Keszthelyi, G. Nagy and Kacsóh [31] prepared cubic ice by pressurizing the vessel containing equeous ferrous perchlorate solution, and they demonstrated that the presence of cubic ice in the specimens prepared this way did not affect the Mössbauer spectra of the ferrous ions. Ruby, Barnabei and Zabransky [32] observed that the temperature at which $FeCl_2 \cdot 9H_2O$ recrystallizes from solution in heavy water increases by 22 ^{o}K relative to a normal aqueous solution. The explanation for this strong deuterium isotope effect was not given. The effect of heavy water on the delay of the crystallization can also be inferred from ref. [33], in which no recrystallization of $FeCl_2$ hydrate was observed even after keeping the sample for a long period /$\sim$ 10 hours/ at higher temperatures. It seems that the formation of stable $FeCl_2 \cdot 9D_2O$ nuclei probably requires a higher activation energy than $FeCl_2 \cdot 9H_2O$.

Goldanskii et al. [34] investigated the effect of structural transformation in glassy monomeric dimethacrylate butanediol /DMBD/ on the Mössbauer parameters of $FeCl_3$ frozen in DMBD.They observed that the Mössbauer effect intensity dropped below the transition point but then increased sharply at the transition temperature. Moreover the shape of the spectrum changed below T_c, the hyperfine splitting disappearing due to the acceleration of spin lattice relaxation.

In a study of the solvent effect on SnI_4 in various frozen solutions Vértes and Burger [35] demonstrated that a correlation exists between the isomer shift of Sn^{4+} and the solvent donor number the concept introduced by Gutmann [36]. The number of electrons in the 5d shell of tin could be estimated from the experimental shift values by assuming that solvation effects only the population of the 5d orbitals. The 5d electron density was

smallest for nitrobenzene and increased in the series nitrobenzene < acetonitryl < acetone < ethylacetate < dimethylformamide < hexamethylphosphoramide. Vértes observed [37] a well-resolved hyperfine-split spectrum of $FeCl_3$ in formamide, and demonstrated that electronic exchange between Fe^{2+} and Fe^{3+} in this system can occur only if some water is present.

4. STUDIES ON FeX_2 (X = Cl, B , I) FROZEN SOLUTIONS AND THEIR CRYSTALLINE HYDRATES

4.1. Frozen solutions.

In the preceeding section emphasis was placed on the necessity of studying solutions of certain groups of compounds. The group chosen for our own investigations was FeX_2 the view of the fact that $FeCl_2$ and its crystalline hydrates have already been investigated thoroughly by Mössbauer effect. Since the structure and phase diagram of the various FeX_2 - water systems could be expected to be the same, it seem a reasonable hope that the effect of the anions on the Fe^{2+} Mössbauer parameters could be investigated too. From the Mössbauer parameters measured in $FeCl_2$ frozen solutions at -90 ^{o}C it had been concluded that a new crystalline hydrate of $FeCl_2$ containing $9H_2O$ exists. As $FeBr_2 \cdot 9H_2O$ and $FeI_2 \cdot 9H_2O$ were already earlier discovered, detailed comparison of the Mössbauer spectra of the three frozen solutions should provide further evidence for the existence of $FeCl_2 \cdot 9H_2O$.

A diagram was prepared which showed relationship between the Mössbauer parameters of $FeCl_2$ hydrated crystals and their hydration number [38]. This diagram gave information on the chemical bond and structure of these compounds, therefore, the increase of the available experimental data for this diagram seemed useful.

In view of the large atomic absorption of Br and I, solution /0,1M/ containing enriched ^{57}Fe bromide and iodide were used. These were prepared by dissolving iron metal /enriched to 80 %/ in hydrobromic and hydroiodic acid.

Frozen samples containing 0.7 mg $^{57}Fe/cm^2$ were measured after quenching in liquid nitrogen and after heating to different temperatures. The characteristic spectra measured at various temperatures are shown in Figs 4 and 5. The temperature dependences of the quadrupole splitting (ΔE), linewidth (Γ) and the intensity of the Mössbauer effect (R) are plotted in Figs. 6 and 7.

The very similar spectra for ferrous bromide and iodide show a quadrupole-split line pattern at liquid nitrogen temperature and below the

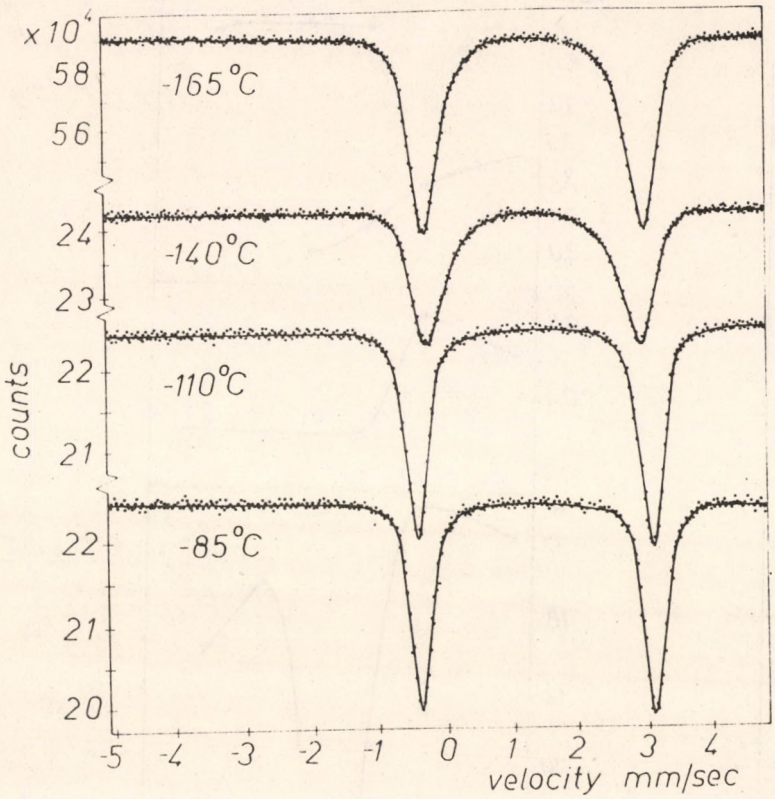

Fig. 4

Mössbauer spectra of $FeBr_2$ frozen solutions.

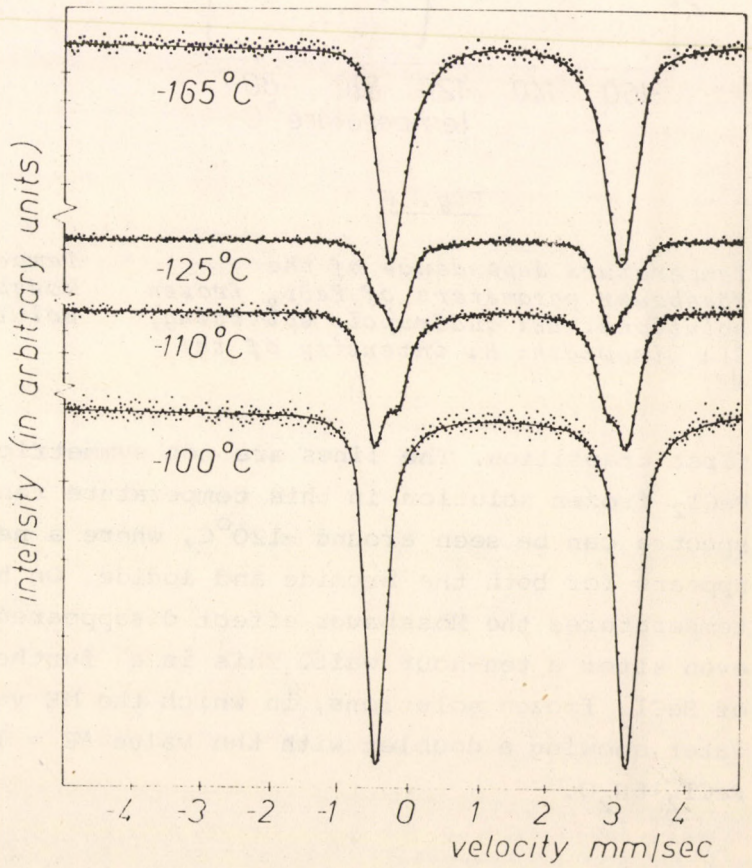

Fig. 5

Mössbauer spectra of FeI_2 frozen solutions.

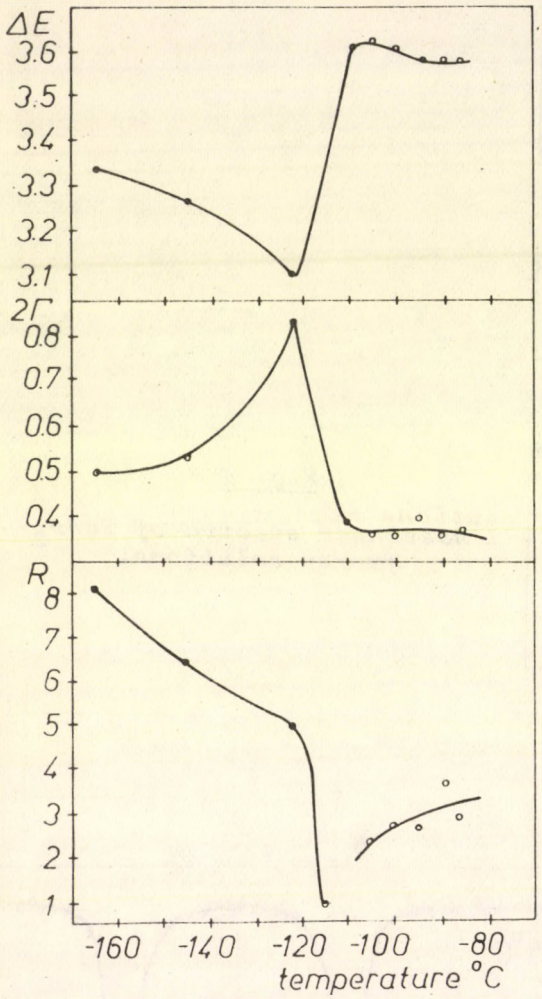

Fig. 6

Temperature dependence of the Mössbauer parameters of $FeBr_2$ frozen solutions. ΔE: quadrupole splitting; 2Γ: linewidth: R: intensity of the ME.

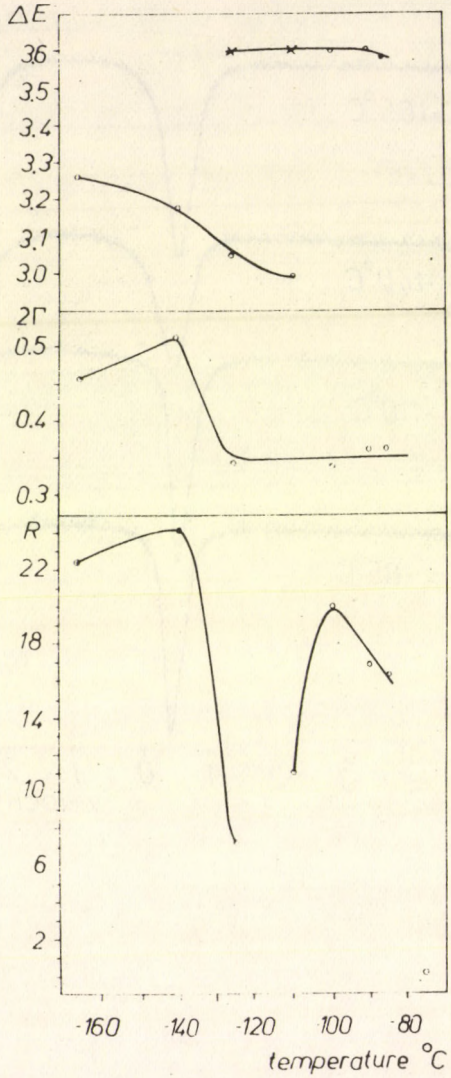

Fig. 7

Temperature dependence of the Mössbauer parameters of FeI_2 frozen solutions.

first transition. The lines are not symmetric, as was observed earlier for $FeCl_2$ frozen solution in this temperature range [15,29,32]. A change of the spectra can be seen around -120°C, where a new doublet with ΔE = 3,6 mm/sec appears for both the bromide and iodide. On heating the sample to higher temperatures the Mössbauer effect disappeared at -75° and it did not reappear even after a ten-hour wait. This is a further difference from the behaviour of $FeCl_2$ frozen solutions, in which the ME vanished at -60°C but reappeared later showing a doublet with the value ΔE = 1,8 mm/sec characteristic of $FeCl_2 \cdot 6H_2O$.

In water-glycerol solution the segregation of clustering of the solute salt can be prevented [28,38,39]. Samples prepared in 1:1 water-glycerol solution were found to give Mössbauer spectra very similar to those of frozen aqueous solution measured at the same /-165°C/ temperature. The δ, ΔE and Γ values are listed in Table I. Since the spectra measured below -120°C could not be fitted to Lorentzian lines, the values were obtained in the following way. The outer profile of the absorption lines was used to construct a hypothetical line. The distances between two hypothetical lines were adopted as ΔE, for δ the center of symmetry of the two lines were used while Γ was measured at the half height of the asymmetrical lines.

Table I

Mössbauer parameters of FeX_2 frozen solutions measured directly after quenching to -165°C /o - aqueous, x - 1:1 water-glycerol solution./ Errors: ± 0.05 mm/sec

Simple	δ *mm/sec*	ΔE *mm/sec*	Γ *mm/sec*
$FeCl_2$ o	1.30	3.10	0.55
" *	1.35	3.30	0.40
$FeBr_2$ o	1.35	3.25	0.50
" *	1.35	3.30	0.40
FeI_2 o	1.35	3.25	0.45
" *	1.35	3.30	0.40

The very lose δ and ΔE values listed in the Table suggest that the structure around the Fe^{2+} ions is the same in all these frozen aqueous systems and that the different anions have no effect. It can be concluded therefore, that the Fe^{2+} ions are probably surrounded by water molecules. Moreover, the lack of difference between the δ and ΔE values for the aqueous and water-glycerol systems supports the view that in frozen aqueous solutions the solute ions are in fact in a glassy phase. Because of the structural disorder, a broadening of the lines occurs though the degree of disordering is not high enough to alter the ground state of the ferrous ion. If there were any change, then ΔE values of 2,0 mm/sec would have

been observed corresponding to an electric field gradient of 2/7 $\langle r^{-3} \rangle$ a.u.

On heating the frozen samples, ΔE, R, and Γ changed abruptly near -120°C. This is the characteristic behaviour already observed in other frozen ferrous salt solutions - the glassy phase melts and the recrystallization of a hydrated ferrous salt takes place. In ferrous bromide and iodide solutions, the recrystallisation occurs simultaneously with the melting. During the measuring time /4 hours/ the coexistence of the old and the new phase was observed /Fig. 5/. The new phase consists of $FeX_2 \cdot 9H_2O$, which is the stable phase of FeX_2-water system in this temperature range. This compund probably forms a eutectic with some ice and this eutectic melts at -75°C, where the Mössbauer effect disappears. It is interesting that if the sample was recooled from -70°C to -85°C the spectrum with $\Delta E \sim 3.6$ mm/sec reappeared gradually over a period of about 4 hours. In the first hour this spectrum showed a doublet of high asymmetry in the relative intensity of lines, which can be atributed to preferential orientation or - less likely - to the Goldanskii-Karyagin effect.

4.2. Crystalline hydrates.

The parallel study of the crystalline hydrates of the compounds examined in frozen solutions is necessary because of the appearance of the hydrated crystals in various temperature ranges. For example, it could be convincingly shown that line due to $FeCl_2 \cdot 6H_2O$ appear in the spectrum of $FeCl_2$ frozen solution [41]. On the other hand, the proof of the presence of $FeCl_2 \cdot 9H_2O$, could not be given directly as it was in the case of hexahydrate, because the synthesis of the nonahydrate is extremly difficult and, indeed, has yet to succeed. Nevertheless, it constitutes indirect evidence for the existence of $FeCl_2 \cdot 9H_2O$ that the value ΔE = 3,6 mm/sec also appears in the spectrum of $FeBr_2$ and FeI_2. The $FeBr_2$ and FeI_2 nonahydrates have already been synthesized. The different hydrated salts containing six and nine water molecules already synthesized are listed in Table II along with the temperature intervals in which they are stable [42].

Table II

Temperature stability of FeX_2 /X = Cl,Br,I/ hexa- and nonahydrates

compound	*Temperature /°C/*
$FeCl_2 \cdot 6H_2O$	< 9
$FeBr_2 \cdot 6H_2O$	-22 ... 48
$FeI_2 \cdot 6H_2O$	< 10 or room temp. in vacuo
$FeBr_2 \cdot 9H_2O$	< -34
$FeI_2 \cdot 9H_2O$	< -30

In fact, ΔE = 3,6 mm/sec does indeed appear in the spectra of $FeBr_2$ and FeI_2 frozen solutions. As can be seen from Table III. the δ, ΔE and Γ values are the same for all three samples.
As well as confirming the presence of the nonahydrates this also suggests that the crystals are probable isomorphs and that the nearest neighbours of the ferrous ions consist only of water molecules.

Table III

Mössbauer parameters of frozen solutions of FeX_2 /X=Cl, Br, I/ at -85°C.
Errors: $\Delta\delta = \pm 0.02$, $\Delta/\Delta E/ = \pm 0.01$, $\Delta\Gamma = \pm 0.01$ mm/sec.

Samples	δ *mm/sec*	ΔE *mm/sec*	Γ *mm/sec*
$FeCl_2$ - *f.s.*	1,31	3,60	0,32
$FeBr_2$ "	1,31	3,58	0.34
FeI_2 "	1,31	3,58	0,36

FeX_2(X = Br, I)$6H_2O$ hydrated crystals were synthesized using the following method. An aqueous solution of $FeBr_2$ or FeI_2 was kept at a temperature where these hexahydrates are stable. The salts crystallized out from the solution at these temperatures. The derivatograms of the compounds confirmed their composition. The derivatogram of $FeBr_2 \cdot 6H_2O$ is shown in Fig. 8. The six peaks corresponding to the six water molecules can be seen on the DTG curves.

The Mössbauer spectra of $FeBr_2 \cdot 6H_2O$ measured at various temperatures are shown in Fig.9. An interesting change of the spectra can be seen. Two quadrupole-split spectra, one with ΔE = 3.0, the other with ΔE = 2.2, could be observed. The δ values were the same for both spectra.

In an interval of 200 °K both spectra appeared, but below -20°C and above only one proved to be stable. For example, if the sample was kept at room temperature for about 12 hours then one quadrupole doublet existed with ΔE = 3.0 mm/sec. If the sample was kept at -25°C, then the other phase appeared to be stable. But if the sample was cooled quickly through this temperature the room-temperature phase could be frozen down to -196°C.

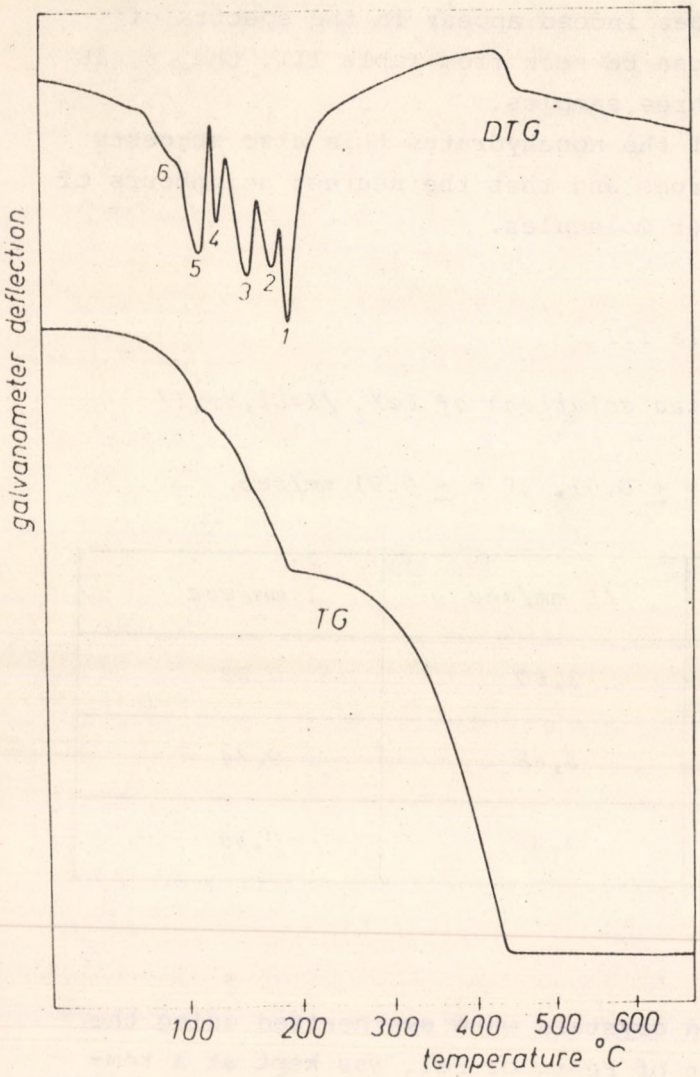

Fig. 8

Derivatogram of $FeBr_2 \cdot 6H_2O$ TG.; thermogravimetric curve DTA.; differential thermogravimetric curve

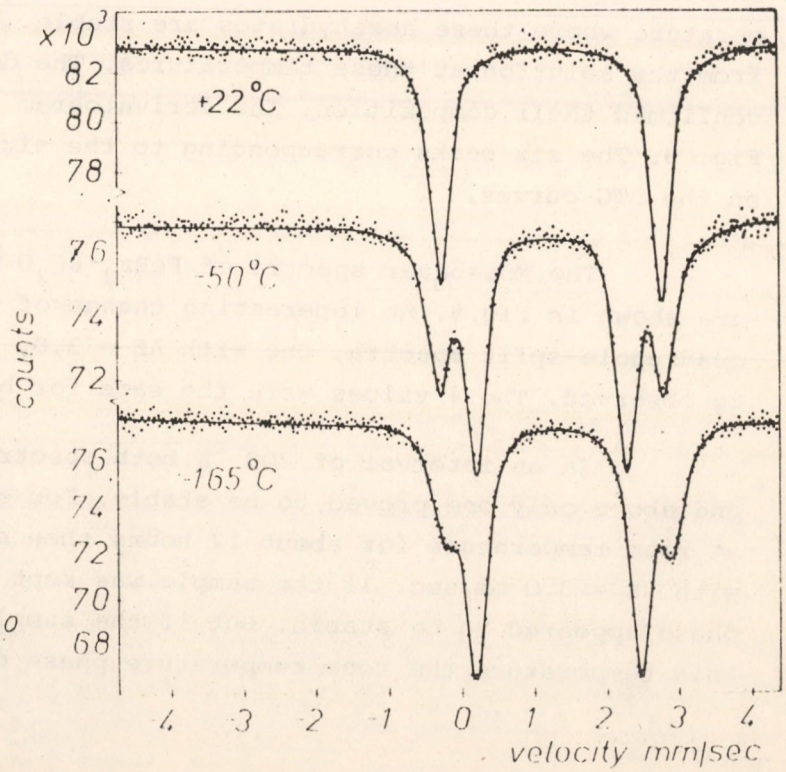

Fig. 9

Mössbauer spectra of $FeBr_2 \cdot 6H_2O$

$FeI_2 \cdot 6H_2O$ showed a quadrupole-split Mössbauer spectra, but no similar change could be seen as was in $FeBr_2 \cdot 6H_2O$. The δ, ΔE and Γ values are compiled in Table IV.

Table IV

The Mössbauer parameters of $FeX_2 \cdot 6H_2O$ compounds

Sample	δ *mm/sec*	ΔE *mm/sec*	Γ *mm/sec*	*T °K*
$FeCl_2 \cdot 6H_2O$	1.37	1.81	0.33	108
	1.30	1.60	0.35	280
$FeBr_2 \cdot 6H_2O$	1.36	3.04	0.37	108
	1.35	2.18	0.33	
	1.25	2.92	0.29	300
	1.26	1.88	0.29	
$FeI_2 \cdot 6H_2O$	1.27	2.98	0.33	108
	1.21	2.72	0.30	300

The values of δ support the presence of high-spin ferrous iron in these compounds. For high-spin ferrous ions the expression for the quadrupole splitting /ΔE/ is [42]

$$\Delta E(T) = \frac{2}{7} e^2 Q(1 - R)\alpha^2 < r^{-3} >_o F(\Delta_1 \Delta_2 \alpha^2 \lambda_o T)$$

Where Q is the quadrupole moment of the excited state of the ^{57}Fe nuclei, (1-R) is the Sternheimer antishielding factor, and α^2 is the covalency factor. F is dependent on the crystalline field splitting (Δ_1, Δ_2), the spin orbit coupling constants $(\lambda_o \alpha^2)$ and the temperature(T). In the special case when the crystalline field has an axial symmetry and the ground state is composed of an equal mixture of d_{xz} and d_{yz} states $(\Delta_1 = \Delta_2)$, then F = 1/2. If the singlet orbital is in the ground state, then F = 1 at low T. Using the values for Q, α^2,(1-R) and λ_o given in ref. [43], ΔE can take have two values: 4.1 and 2.05 mm/sec. The later realises in the case of $FeCl_2 \cdot 6H_2O$ [41], and both e.g. in $Fe(ClO_4) \cdot 6H_2O$, depending on the temperature [44]. The lower ΔE value can be observed in $FeCl_2$ and $FeBr_2$ hexahydrates. The ΔE = 3.0 mm/sec value was measured in $FeCl_2 \cdot 4H_2O$ but it would be too risky to attribute this value unequivocally to the structure observed in $FeCl_2 \cdot 4H_2O$.

The value of δ decreases from Cl to I showing the difference of the electronegativity of these anions. In contrast to the nonahydrates, for

hexahydrates a significant effect of the anions to the isomer shift can be observed. This suggests that the halogen ions in hexahydrate are probably coordinated to the ferrous ions.

5. STUDIES ON SOME FROZEN SOLUTIONS OF HEXA AND PENTA CYANOFERRATE COMPLEXES

5.1. Frozen solutions of $Na_4[Fe(CN)]_6$, $K_3[Fe(CN)]_6$ and $Na_3[Fe(CN)]_6$.

Frozen solutions containing compounds of low-spin ferrous ions were investigated by Mundt and Sonnino [45] and Domingues and Danon [46]. They showed a definite effect of the lattice on the hyperfine parameters of low spin ferrous ions. We intended to extend these studies to the water - glycerol frozen solutions. For intercomparison of the data we mesured the Mössbauer spectra of the pure compound in solid phase, in frozen water and in a frozen 1:1 water-glycerol solution of the complexes.
The Mössbauer spectrum of $Na_4[Fe(CN)]_6$ displayed a single unsplit line for each samples. The $K_3[Fe(CN)]_6$ samples displayed a quadrupole-split spectrum. The δ , ΔE and Γ values are listed in Table V. The spectra were measured at -165 ^{o}C.

Table V

Mössbauer parameters of hexacyanoferrate complexes.
0,5 M% concentrations

The sample	δ (*mm/sec*)	ΔE (*mm/sec*)	Γ (*mm/sec*)
$Na_4[Fe(Cn)_6]\cdot 10H_2O$	-0.024	-	0.40
aqueous solution	-0.021	-	0.40
glycerol added	-0.019		0.36
$K_3[Fe(CN)]_6$	-0.062	0.36	0.38
aqueous solution	-0.060	0.49	0.44
glycerol added	-0.066	0.81	0.50

Errors; $\Delta\delta = \pm 0.008$; $\Delta(\Delta E) = \pm 0.005$; $\Delta\Gamma = \pm 0.005$ *mm/sec*
δ *values are relative to metallic iron. Source:* $^{57}Co(Cr)$

A very small difference in the line width measured in $Na_4[Fe(CN)_6]$ and water -glycerol solution can be attributed to the change of the value of the unresolved quadrupole splitting observed in this compound [47]. The ΔE and δ parameters differ for $K_3[Fe(CN)_6]$ solid and solutions. This can be explained as follows. In aqueous solutions the solute complexes segregate and, therefore the same or almost the same Mössbauer spectra can be found as it is in the pure solid complexes. In solutions containing glycerol the segregation is prevented. Therefore, the spectra can be attributed to the complex ions. It seems that the cations bound to the complex ions decrease the electric field gradient. The segregation in $K_3[Fe(CN)]_6$ frozen aqueous solution is partial because the ΔE and Γ value lie in beetwen the values of pure complex and frozen glycerol solution.

The decrease of the quadrupole splitting could be explaned by the polarisation effect of Na^+ ions to the CN^- groups. If water dipoles are near to CN^- ions instead of Na^+, the CN^- groups withdraws less electrons from the iron ion, consequently the electric field gradient increases. These results show that the indirect lattice contribution to the electric field gradient in these complexes can not be neglected.

5.2. Studies on pentacyanoferrates.

The pentacyanoferrates $Na_3[Fe(CN)_5H_2O]$ and $Na_2[Fe(CN)_5H_2O]$ are not stable in aqueous solution. Emschwiller [48] explained the changes of the chemical activity of $Na_3[Fe(CN)_5H_2O]$ in aqueous solution by the dimerisation of the aquopentacyanoferrate ions. The optical spectra of solutions of this ion show defined changes [49]. These changes have generally been explained by the existence of dimer molecules containing two cyanide bridges. The investigations of their chemical reactions were not made by other physical method, which could confirm the explanation outlined above.

Aquopentacyanoferrate (II) and (III) was prepared by the method of Hofmann [50]. The composition of the complexes were checked by chemical analysis.

The Mössbauer spectrum of these complexes consisted of one doublet. The δ, ΔE and Γ values are listed in Table VI.

Table VI

Mössbauer parameters of $Na_3[Fe(CN)_5 \cdot H_2O] \cdot 2H_2O$ and $Na_2[Fe(CN)_5 \cdot H_2O]$ according to Hofmann [50] Source: $^{57}Co(Cr)$. Errors: 0,005 mm/sec.

Sample	δ (mm/sec)	ΔE (mm/sec)	Γ (mm/sec)	T (°C)
$Na_3[Fe(CN)_5H_2O] \cdot 2H_2O$	0,035	0,757	0,345	20
$Na_2[Fe(CN)_5H_2O]$	-0,029	2,064	0,54	-165

The aquopentacyanoferrate (II) values are in good agreement with the values given in ref. [51] and [52].

Table VII

Mössbauer parameters of aquopentacyanoferrate (II) and (III) frozen aqueous solutions. (A): fresly prepared solutions; (B): samples left standing 1 day.

Errors; ± 0.01 mm/sec. pH = 13.

Sample	δ (mm/sec)	ΔE (mm/sec)	Γ (mm/sec)
$Na_3[Fe(CN)_5H_2O]$ Solid. T =-165°C	0,085	0,78	0,40
" A	0,07	0,78	0,36
" B	-0,02*	-	0,33
$Na_4[Fe(CN)]_6$ f.s.	-0,02*	-	0,43
$Na_2[Fe(CN)_5H_2O]$ Solid. T =-165°C	-0,03	2,06	0,54
A	-0,02	2,13	0,60
	-0,02	2,4	0,70
	-0,015*	-	0,40

* *single lines.*

These complexes contains low spin iron ions.

Aqueous solutions were prepared with 40 mg/ml complex concentration. Two series of measurements were made. In one, the freshly prepared solutions were frozen, and in the other the solutions were kept in CO_2 atmosphere for one day at room temperature. Two Mössbauer spectra of each series of $Na_3[(CN)_5H_2O]$ solutions are shown in Fig. 10, and two characteristic spectra of $Na_2[Fe(CN)_5\ H_2O]$ frozen solutions can be seen in Fig. 11. The Mössbauer spectra of the samples left standing 1 day are different from the freshly prepared ones. The characteristic parameters are listed in Table VII. For comparison the table shows the values measured for sodium hexacyanoferrate aqueous solutions.

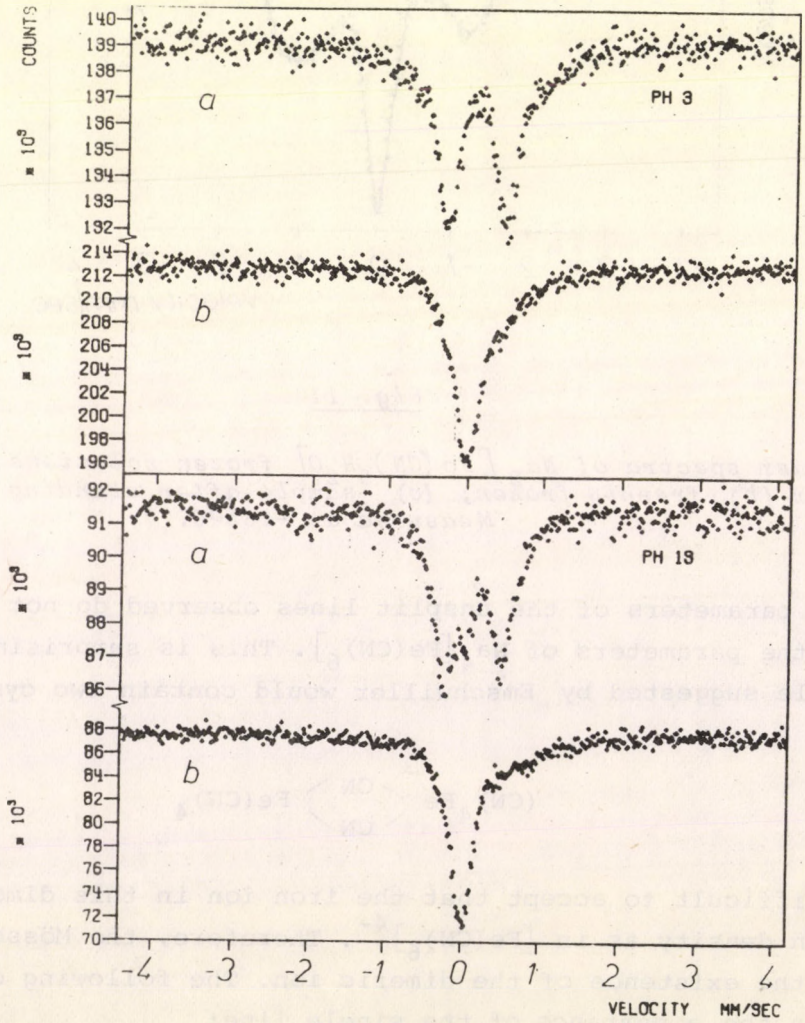

Fig. 10

Mössbauer spectra of $Na_3[(Fe(CN)_5H_2O]$ frozen solutions. (a) freshly frozen samples (b) samples after standing 1 day. Measured at -165°C

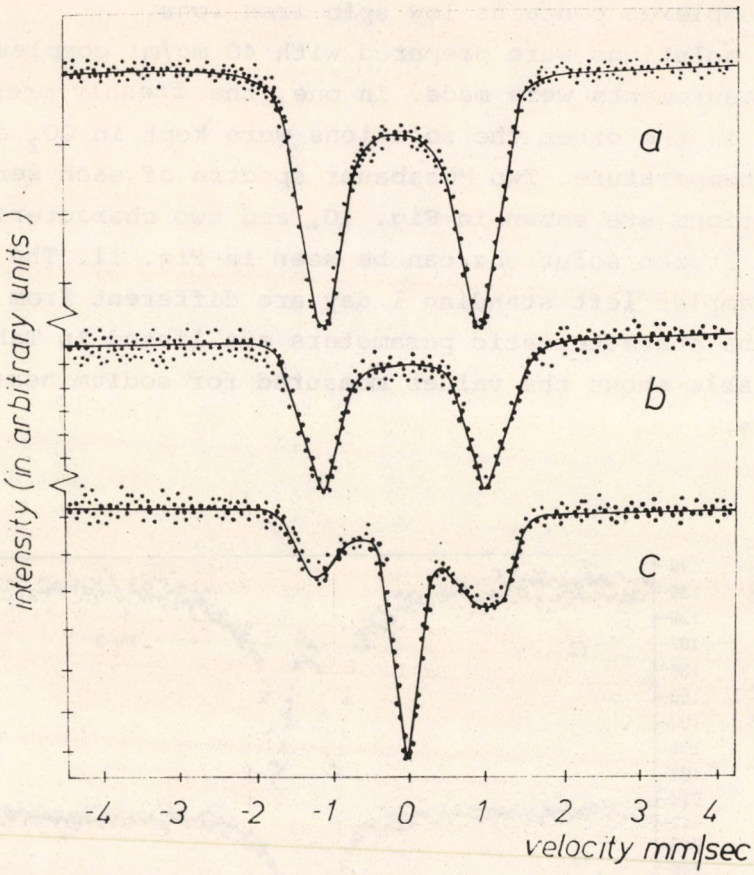

Fig. 11

Mössbauer spectra of $Na_2[Fe(CN)_5H_2O]$ frozen solutions (a) solid complex (b) freshly frozen; (c) sample after standing 1 day. Measured at -165°C.

The parameters of the unsplit lines observed do not differ significantly from the parameters of $Na_4[Fe(CN)_6]$. This is surprising because the dimer molecule suggested by Emschwiller would contain two cyanide bridges:

$$(CN)_4Fe \begin{matrix} \diagup CN \diagdown \\ \diagdown CN \diagup \end{matrix} Fe(CN)_4$$

It is very difficult to accept that the iron ion in this dimer would have the same electron density as in $[Fe(CN)_6]^{4-}$. Therefore, the Mössbauer spectra do not confirm the existence of the dimeric ion. The following chemical reaction could explain the appearance of the single line:

$$6[Fe(CN)_5H_2O]^{3-} + 2OH^- \rightarrow 5[Fe(CN)_6]^{4-} + Fe(OH)_2 + 6H_2O$$

The $Fe(OH)_2$ can apparently be oxidized to $Fe(OH)_3$ as a resonance absorption which could be attributed to the latter can be seen on the Mössbauer spectra of the solutions. The ΔE value of $Fe(OH)_3$ sol was found to be 0,70 mm/sec [53].

Also the δ and ΔE values of the single line observed in $Na_2[Fe(CN)_5H_2O]$ frozen solution the same as of the $Na_4[Fe(CN)_6]$ frozen solution. The reduction of the hexacyanoferrate (III) complex ion to hexacyanoferrate (II) in basic solutions is well known. It seems that the reduction also takes place in basic aquopentacyanoferrate (III) solutions.

6. CONCLUSIONS

The apparently anomalous phenomena observed earlier in the Mössbauer spectra of frozen solutions could be satisfactorily explained by the parallel application of Mössbauer effect, thermal analysis and other physical methods. It was found that during the cooling process the solute ions segregate or cluster from the solution at relatively low concentrations. At least two phases could be formed: (1) Glassy phase which was observed in ferrous salt solutions (2) Hydrated crystal segregation, observed, for example, in ferrous cyanide frozen solutions. The sizes of the segregated phases are not known. Some solute ions may occur in pockets distributed in the bulk ice or they may be located in between ice - crystal boundaries. The frozen samples solidify into perfectly glassy state /the ice do not crystallise out/ if glass formers /glycerol, etc./ are added to the equeous solution or the solutions made with glass-forming solvents /e.g. alcohols, dimethylformamide, etc./. The glass transition characteristic of solid glasses can be observed through the changes of the Mössbauer parameters.

The appearance of some hydrated salts can be observed in some cases after the recrystallization process has taken place in melted glass. In some frozen solution the recrystallization takes very long time /days/.

The recrystallised salts forms solid eutectic with highly dispersed ice crystals. The quantity of ice which melts with the glass is not known but some of it probably recrystallizes simultaneously with the melting of the glass. By the measurement the heat evolved during the glass transition the quantity could be estimated.

Ionic structures in some solutions could be successfully investigated by Mössbauer spectroscopy of the frozen solution samples.

It seems that the studies can be successfully extended to the following areas:

- Study of glass transitions.
- Investigation of paramagnetic relaxation in dilute frozen systems. /The clustering of paramagnetic ions may not to be neglected if glass former is not added to the solution/.
- Study of the ionic structures in solutions. Determination of phase diagrams.
- Study of solid state polymerisation.
- Investigation of solvent effects.
- Observation of chemical reactions in solutions.

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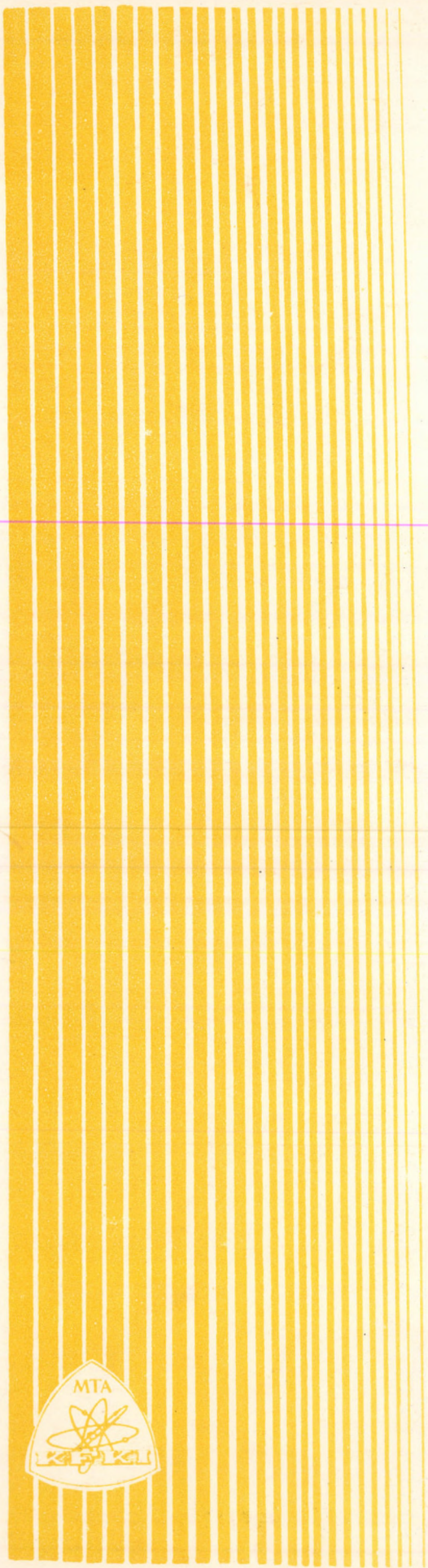

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